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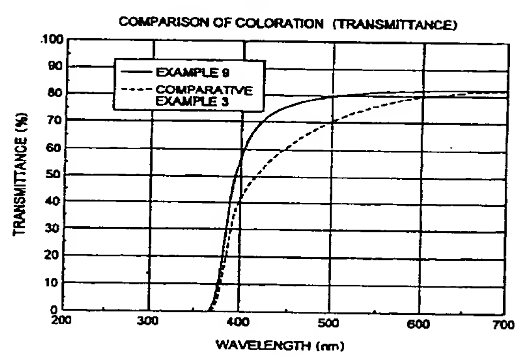
(54) **Optical glass for precision molding**

(57) An optical glass for precision molding, having excellent properties, i.e. yield temperature (At) of at most 550 °C, refractive index (nd) of at least 1.83 and Abbe number (vd) of at most 26.0 and further providing low softening as well as improved mass production capability with less coloration, which is represented, in term of atoms for making up the glass, by the following chemical composition (wt %):

P_2O_5	14.0 to 31.0 %
B_2O_3	0 to 5.0 %
GeO_2	0 to 14.0 %
Sum of $P_2O_5 + B_2O_3 + GeO_2$	14.0 to 35.0 %
Li_2O	0 to 6.0 %
Na_2O	2.5 to 14.0 %
Sum of $Li_2O + Na_2O$	2.5 to 15.0 %
Nb_2O_5	22.0 to 50.0 %
WO_3	0 to 30.0 %
Bi_2O_3	5.0 to 36.0 %
BaO	0 to 22.0 %

FIG. 1



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Description

[0001] This invention relates to an optical glass for precision molding, capable of being precision molded at a low temperature and needing no polishing and grinding after the precision molding.

[0002] Since prior art optical glass of the SF type (high refractive index, high dispersion) containing a large amount of lead oxide in the glass composition is very stable and has a relatively low softening point, its precision molding thereof is carried out in a low temperature range. JP-A-1-308843 describes a glass composition rendered feasible at a further low temperature as an optical glass for precision molding. JP-A-7-247135 and JP-A-7-247136 describe glasses of P_2O_5-PbO-Nb_2O_5-WO_3-alkali metal oxide type each containing a large amount of lead oxide and JP-A-8-157231 describes P_2O_5-B_2O_3-Nb_2O_5-WO_3-alkali metal oxide type glasses.

[0003] However, precision molding is generally carried out in a reducing atmosphere so as to prevent a mold from oxidation, so if lead oxide is contained in the glass composition, the lead oxide on the glass surface is reduced and deposited as lead on the surface of a precision molding lens. The lead is evaporated by heating for the precision molding, a part of which adheres to the surface of the mold material to form a convex part which is then transferred to the surface of the precision molding lens as it is. When such steps are continuously repeated, the surface accuracy of the precision molding lens cannot be maintained, so that not only such optical properties as designed can not be obtained, but also an operation for removing the lead adhered to the mold is required. This is not suitable for mass production of lenses. Furthermore, because lead oxide is contained in large amounts, the specific gravity is increased and thus, there arises another problem that it is difficult to reduce the weight of an optical part in which these lenses are incorporated. Accordingly, the glasses described in the foregoing JP-A-1-308843, JP-A-7-247135 and JP-A-7-247136 are not suitable, nor practically used as an optical glass for precision molding.

[0004] On the other hand, in a glass as described in JP-A-8-157231, certainly lead oxide is not incorporated, but in place of the lead oxide, TiO_2 is always incorporated, although claimed as an optimal component, in order to obtain high refractive index, high dispersion properties as shown in Examples 7 to 11 of the second embodiment of the present invention. Consequently, the resulting glass is very strongly colored. In ordinary optical systems, use of a single glass lens is not realistic and many optical systems are actually composed of a number of lenses. Thus, it is desired that coloration of these glass lenses is reduced as much as possible. Accordingly, the glass described in JP-A-8-157231 is actually caused to have high refractive index, high dispersion properties by TiO_2, which cannot be said to be preferable from the standpoint of optical designing.

[0005] In the case of known mold materials for precision molding, there arises a problem that the higher the precision molding temperature, the more oxidation or deterioration of the mold material occurs, thus resulting in difficulty in maintenance of the surface accuracy of the mold material and in mass production of lenses by precision molding. On the other hand, the precision molding is generally carried out at a temperature higher by 15 to 50°C than the yield temperature (At) of the glass. That is, an optical glass to be subjected to precision molding must be precision molded at a temperature as low as possible and to this end, it is desired that the yield temperature (At) measured by TMA of the glass is as low as possible. In the foregoing JP-A-8-157231, however, there are no examples of a glass having high refractive index, high dispersion properties (refractive index (nd) at least 1.83, Abbe number (νd) at most 26.0) and low softening property (yield temperature (At) at most 550 °C). In this specification, the yield temperature is defined based on measurement by TMA.

[0006] Moreover, the inventors have developed an invention relating to a new optical glass in JP-A-10-316448. In the optical glass of P_2O_5-Nb_2O_5-TeO_2-alkali metal oxide type, described in JP-A-10-316448, the inventors' expected objects can substantially be achieved, but in view of influences upon the ambient environment or the human body by TeO_2 contained in a glass composition, it is concluded that further improvements are required.

[0007] It is an object of the present invention to provide an optical glass for precision molding, capable of being precision molded at a low temperature, without needing polishing and grinding after the precision molding, whereby the above described problems of the prior art can be solved.

[0008] It is another object of the present invention to provide a high refractive index, high dispersion optical glass for precision molding, having excellent properties, i.e. refractive index (nd) of at least 1.83, Abbe number (νd) of at most 26.0 and effect of readily lowering the softening point of the glass such as by lead oxide or tellurium oxide, and further providing a low softening property as shown by a yield temperature (At) of at most 550° C as well as improved mass production capability without being colored.

[0009] These objects can be attained by an optical glass for precision molding, in which P_2O_5, Nb_2O_5, Bi_2O_3 and Na_2O are defined in the specified ranges shown hereafter.

[0010] In the drawing:

Fig. 1 is a graph showing the relationship between the wavelength (nm) and transmittance (%) for comparison of the coloration (transmittance) of optical glasses of Example 9 according to the present invention and Comparative Example 3.

[0011] Specifically, according to the present invention, there is provided a high refractive index, high dispersion optical glass for precision molding, having excellent properties, i.e. refractive index (nd) of at least 1.83, preferably 1.835 to 1.900, Abbe number (vd) of at most 26.0, preferably 25.0 to 21.0 and further providing a low softening property shown by a yield temperature (At) of at most 550 °C, preferably at most 540 °C as well as an improved mass production capability without being colored.

[0012] In particular, the present invention relates to a high refractive index, high dispersion optical glass for precision molding, which is represented, in term of atoms for making up the glass, by the following chemical composition (wt %):

		Preferred Range
P_2O_5	14.0 to 31.0 %	15.0 to 30.0 %
B_2O_3	0 to 5.0 %	0 to 4.0 %
GeO_2	0 to 14.0 %	0 to 12.0 %
Sum of $P_2O_5 + B_2O_3 + GeO_2$	14.0 to 35.0 %	17.0 to 30.0 %
Li_2O	0 to 6.0 %	0 to 5.0 %
Na_2O	2.5 to 14.0 %	5.0 to 13.0 %
Sum of $Li_2O + Na_2O$	2.5 to 15.0 %	5.0 to 14.0 %
Nb_2O_5	22.0 to 50.0 %	25.0 to 45.0 %
WO_3	0 to 30.0 %	0 to 20.0 %
Bi_2O_3	5.0 to 36.0 %	6.0 to 30.0 %
BaO	0 to 22.0 %	0 to 15.0 %

[0013] The reasons for limiting the composition range (% is to be taken as by weight unless otherwise indicated) of each component of this optical glass according to the present invention are as follows:

[0014] P_2O_5 is an essential component for the optical glass according to the present invention and a main component for forming a network structure of the glass, which is present in a proportion of 14.0 to 31.0 %, since if more than 31 %, the yield temperature (At) rises, while if less than 14 %, the devitrification tendency is increased so as to render the glass unstable. The preferred range is 15.0 to 30.0 %.

[0015] B_2O_3 is an optional component but an effective component for forming a network structure similar to P_2O_5 and rendering uniform the glass using a suitable amount, which is present in a proportion of 0 to 5.0 %, since if more than 5.0 %, the desired low yield temperature (At) and high refractive index, high dispersion properties cannot be attained. The preferred range is 0 to 4.0 %.

[0016] GeO_2 is an optional, but very effective component for forming a network structure similar to P_2O_5 and increasing the refractive index of the glass. If the amount of GeO_2 exceeds 14 %, the yield temperature (At) is increased. Because the raw material is expensive, use of this material in large amount is not practical for mass production. Accordingly, the content of GeO_2 is in a range of 0 to 14.0 %, preferably 0 to 12.0 %.

[0017] When the sum of $P_2O_5 + B_2O_3 + GeO_2$ exceeds 35 %, the desired refractive index and yield temperature (At) are hard to obtain and when less than 14 %, the glass becomes unstable. Accordingly, the sum of $P_2O_5 + B_2O_3 + GeO_2$ should be in a range of 14.0 to 35.0 %, preferably 17.0 to 30.0 %.

[0018] Li_2O is an optional, but very effective component for lowering the softening point of the glass in a similar manner to Na_2O. If using Li_2O in a suitable amount with Na_2O, a desired low yield temperature (At) can be obtained. If exceeding 6 %, however, the coefficient of thermal expansion of the glass is increased and accurate transferring of a lens surface during precision molding is difficult, while water resistance is also reduced. Accordingly, the content of Li_2O is in a range of 0 to 6.0 %, preferably 0 to 5.0 %.

[0019] Na_2O is an essential component for the optical glass according to the present invention and a very important component for largely contributing to the low softening and stability of the glass. If less than 2.5 %, its effects are decreased, while if exceeding 14 %, the water resistance of the glass is reduced. Accordingly, the content of Na_2O should be 2.5 to 14.0 %, preferably 5.0 to 13.0 %.

[0020] When the sum of Li_2O and Na_2O exceeds 15 %, the glass tends to be unstable and the water resistance of the glass is reduced. If less than 2.5 %, the desired low yield temperature (At) cannot be obtained. Accordingly, the sum

of Li_2O and Na_2O should be in a range of 2.5 to 15.0 %, preferably, 5.0 to 14.0 %.

[0021] Nb_2O_5 is an essential component for the optical glass according to the present invention and a very effective component for attaining the desired high refractive index, high dispersion. If less than 22 %, however, the effect is decreased, while if exceeding 50 %, the melting property is markedly deteriorated and the glass is very unstable. Accordingly, the content of Nb_2O_5 should be in a range of 22.0 to 50.0 %, preferably 25.0 to 45.0 %.

[0022] WO_3 is an optional component but an effective component for attaining the desired high refractive index, high dispersion properties according to the present invention, similar to Nb_2O_5, and for controlling the refractive index without raising the yield temperature (At) by using in a suitable amount with Nb_2O_5. If exceeding 30 %, however, the water resistance of the glass is reduced and the specific gravity of the glass tends to be increased. Accordingly, the content of WO_3 should be in a range of 0 to 30.0 %, preferably 0 to 20.0 %.

[0023] Bi_2O_3 is an essential component for the optical glass according to the present invention and a very important component for lowering the yield temperature (At) in a similar manner to alkali metal oxides as well as raising the refractive index of the glass in a similar manner to Nb_2O_5, and WO_3. If less than 5 %, however, the effect is decreased, while if exceeding 36 %, the specific gravity of the glass tends to be increased and noble metals of the melting container tend to be attacked thereby coloring the glass. Accordingly, the content of Bi_2O_3 should be in a range of 5.0 to 36.0 %, preferably 6.0 to 30.0 %.

[0024] BaO is an optional component but an effective component for controlling the refractive index. If exceeding 22 %, the high refractive index is hard to maintain and the glass is unstable. Accordingly, the content of BaO should be in a range of 0 to 22.0 %, preferably 0 to 15.0 %.

[0025] In the optical glass of the present invention, in addition to the above described components, ZrO_2, Ta_2O_5, Ga_2O_3, K_2O, MgO, ZnO, CaO, and SrO, can be incorporated for the purpose of controlling the optical constants, improving the melting property and increasing the stability of the glass without departure from the scope of the present invention.

[0026] Production of the optical glass according to the present invention may be carried out by weighing and mixing the corresponding raw material compounds so that a predetermined proportion of the object composition is given, for example, oxides, hydroxides, carbonates, nitrates and phosphates, adequately blending these materials, charging the resulting mixture in a platinum crucible, melting in an electric furnace at a temperature of 900 to 1200 °C with suitable agitation to render homogeneous, cleaning and casting the mixture in a preheated metallic mold at a suitable temperature and then gradually cooling. A small amount of a defoaming agent such as Sb_2O_3, can further be added.

[0027] The following examples are given in order to illustrate the present invention in detail without limiting the same.

Examples 1 to 15

[0028] Examples of compositions (weight %) of the optical glass according to the present invention and their characteristic values of refractive index (nd), Abbe number (νd) and yield temperature (At) are shown in Table 1. The yield temperature (At) was measured by the use of a thermomechanical analyzer whilst raising the temperature at 5 °C per minute.

[0029] Optical glasses of this Example were prepared by using the corresponding oxides, hydroxides, carbonates, nitrates and phosphates as raw materials for each component, weighing these materials to give proportions of compositions as shown in Table 1, adequately mixing, then charging to a platinum crucible, melting in an electric furnace at 900 to 1200 °C, stirring the mixture for a suitable time to render homogeneous, cleaning, then casting into a metallic mold preheated at a suitable temperature and gradually cooling to prepare an optical glass of each Example.

[0030] Then, a glass block with a predetermined weight was cut out of the resulting glass, polished in a columnar shape in conventional manner and subjected, as a preform, to precision molding to obtain several lens articles. These lenses exhibited good transferring property and no adhesion of the glass and evaporated matters to a mold material was found.

Table 1 (wt %)

Composition	Example No. 1	2	3	4	5
P_2O_5	28.7	28.5	23.2	28.3	29.0
B_2O_3	-	1.0	1.1	1.0	-
GeO_2	-	-	6.5	-	1.2
Li_2O	3.8	3.0	4.0	5.8	3.6
Na_2O	5.0	6.2	6.7	2.9	5.2
BaO	-	-	-	-	-
Nb_2O_5	27.7	35.0	47.8	28.5	34.4
WO_3	-	-	-	-	-
Bi_2O_3	34.8	26.3	9.5	33.5	26.6
			SrO 1.2		
Characteristic Values					
nd	1.83960	1.83757	1.85536	1.83679	1.83715
νd	24.6	24.1	23.3	24.9	24.3
At/℃	473	514	544	468	500

Table 1 (wt %) (continued)

Composition	Example No. 6	7	8	9	10
P_2O_5	23.2	17.5	23.4	17.0	24.9
B_2O_3	-	-	2.0	4.0	1.1
GeO_2	-	13.5	-	7.0	-
Li_2O	-	2.7	3.1	3.0	3.5
Na_2O	13.5	7.3	8.2	7.0	5.2
BaO	-	-	-	2.0	-
Nb_2O_5	28.7	37.0	38.7	43.0	29.2
WO_3	-	12.0	11.2	-	-
Bi_2O_3	34.6	10.0	11.2	17.0	34.3
			ZnO 2.2		SrO 1.8
Characteristic Values					
nd	1.83816	1.86320	1.84170	1.88046	1.86251
νd	23.1	23.1	23.3	22.7	23.6
At/℃	512	534	516	520	474

Table 1 (wt %) (continued)

Composition	Example No. 11	12	13	14	15
P_2O_5	15.1	14.5	20.0	23.0	25.1
B_2O_3	1.2	4.5	1.0	-	1.2
GeO_2	6.9	-	-	-	-
Li_2O	6.0	3.0	1.0	3.0	3.4
Na_2O	3.0	3.0	11.0	8.0	5.4
BaO	2.0	22.0	7.0	6.0	-
Nb_2O_5	26.8	31.0	40.0	38.0	28.5
WO_3	28.0	7.0	10.0	12.0	-
Bi_2O_3	11.0	15.0	10.0	10.0	35.1
					MgO 1.3
Characteristic Values					
nd	1.87260	1.85727	1.85271	1.84736	1.85947
νd	23.3	23.0	23.1	23.6	23.7
At/℃	474	547	543	525	476

Comparative Examples 1 to 5

[0031] Glasses of Comparative Examples 1 to 5 correspond to those of Examples 7 to 11, as the second embodiment of the invention described in JP-A-8-157231. In Table 2 are shown the refractive index (nd), Abbe number (νd), yield temperature (At) (which the inventors have actually measured) and coloration (which refers to wavelengths exhibiting transmittance of 70 % and 5 %, represented as a unit of 10 nm through rounding at a decimal place) of these glasses. The measurement method and method of indication of the coloration are according to the Measurement Method of Coloration of Optical Glass in Japanese Optical Glass Industrial Standards (JOGIS 02-1975).

[0032] Generally, the higher the refractive index of the glass, the larger is the reflectivity of light, so that the glass is seen colored in yellow with the naked eye. When TiO_2 is incorporated as a glass component, furthermore, sharp absorption appears in the short wavelength zone and consequently, the resulting glass is further strongly colored. Since all the glasses of Comparative Examples 1 to 5 contain TiO_2, as shown in Table 2, their coloration all exhibit larger values than those of Example 9 in which the highest refractive index, highest dispersion and strongest coloration were given. As exemplified in Fig. 1, the coloration of Example 9 according to the present invention and Comparative Example 3 are respectively 42/37 and 50/38 and the glass of Comparative Example 3 is not preferable as an optical glass for use, because it is more strongly colored than that of Example 9.

[0033] Furthermore, it is well known that when TiO_2 is incorporated in a glass composition, high refractive index, high dispersion properties of the glass composition can readily be obtained. However, the glass containing TiO_2 tends

to exhibit a high yield temperature (At) as is apparent from the data of Comparative Examples showing higher yield temperatures (At) than those of Examples of the present invention. In particular, the glass of Comparative Example 5, having the similar high refractive index, high dispersion properties to those of the present invention as claimed, exhibited a very high yield temperature, i.e. 595 °C. This can be considered due to that, in the composition system of Comparative Examples 1 to 5 (P_2O_5-B_2O_3-Nb_2O_5-WO_3-alkali metal oxides system), it is difficult to incorporate GeO_2 which is considered very effective for increasing the refractive index therein so as to readily obtain high refractive index high dispersion properties and accordingly, there is no way other than to add TiO_2 in addition to the essential components. JP-A-8-157231 discloses that in the composition system P_2O_5-B_2O_3-Nb_2O_5-WO_3-alkali metal oxide, it is difficult to maintain the high refractive index, high dispersion properties when TiO_2 is not added. In the glass of the P_2O_5-Nb_2O_5-Bi_2O_3-Na_2O system the present invention proposes, however, GeO_2 can be incorporated while maintaining the low softening property and it is rendered easy to achieve a high refractive index.

[0034] Based on the above described reasons, none of the glasses of Comparative Examples 1 to 5 can be put to practical use.

Table 2

(wt %)						
Composition	Example 9	Comparative Example No.				
		1	2	3	4	5
P_2O_5	17.0	18.4	23.9	23.4	23.8	27.8
B_2O_3	4.0	12.5	5.6	5.6	2.6	2.6
SiO_2	-	2.0	-	3.0	-	-
GeO_2	7.0	-	-	-	-	-
Li_2O	3.0	1.5	1.0	1.0	3.0	2.0
Na_2O	7.0	10.3	9.5	9.5	5.7	6.7
K_2O	-	-	7.0	7.0	1.5	2.5
TiO_2	-	5.0	9.2	9.2	3.6	8.6
Nb_2O_5	43.0	37.7	33.8	36.8	38.3	39.8
WO_3	-	8.6	7.0	3.0	9.0	5.0
BaO	2.0	0.2	-	-	12.3	5.0
	Bi_2O_3 17.0		SrO 3.0	MgO 1.5	As_2O_3 0.2	
Characteristic Values						
nd	1.88046	1.77071	1.77945	1.77486	1.82818	1.83852
vd	22.7	24.4	26.3	24.1	24.3	21.1
At/°C	520	558	549	564	555	595
Coloration	42/37	49/38	47/38	50/38	43/38	49/38

[0035] According to the present invention, the glass, which the inventors have already proposed in JP A-10-316448, are greatly improved to lower the softening point thereof like lead oxide and tellurium oxide, and on the other hand, there can be provided a high refractive index, high dispersion optical glass for precision molding, containing no components harmful to the ambient environment and health and having excellent properties, i.e. yield temperature (At) of at most 550 °C, refractive index (nd) of at least 1.83 and Abbe number (vd) of at most 26.0 and further providing low softening as well as improved mass production capability with less coloration.

Claims

1. A high refractive index, high dispersion optical glass for precision molding, having a yield temperature (At) of at most 550 °C, refractive index (nd) of at least 1.83 and Abbe number (vd) of at most 26.0, which is represented, in

term of atoms for making up the glass, by the following chemical composition (wt %):

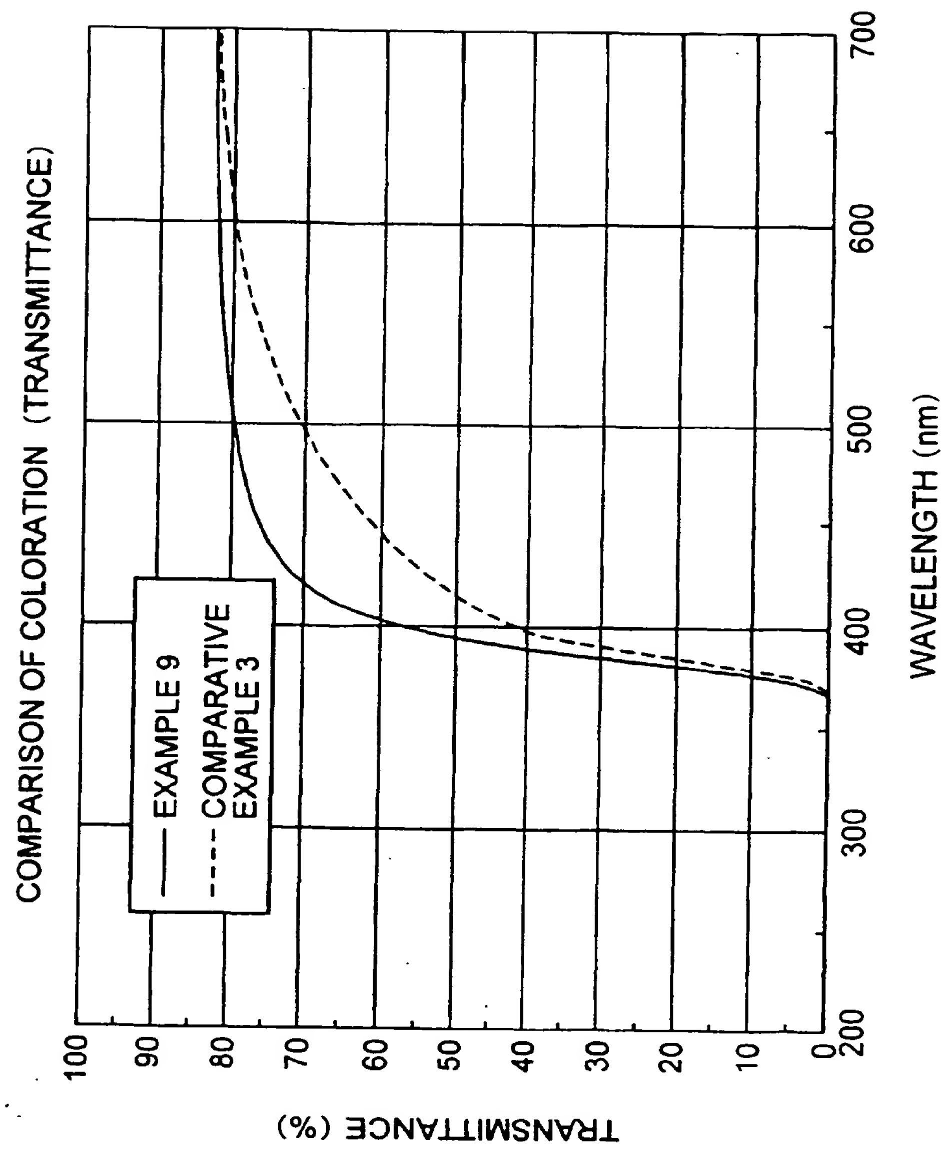
P_2O_5	14.0 to 31.0 %
B_2O_3	0 to 5.0 %
GeO_2	0 to 14.0 %
Sum of $P_2O_5 + B_2O_3 + GeO_2$	14.0 to 35.0 %
Li_2O	0 to 6.0 %
Na_2O	2.5 to 14.0 %
Sum of $Li_2O + Na_2O$	2.5 to 15.0 %
Nb_2O_5	22.0 to 50.0 %
WO_3	0 to 30.0 %
Bi_2O_3	5.0 to 36.0 %
BaO	0 to 22.0 %

2. A high refractive index, high dispersion optical glass for precision molding, having a yield temperature (At) of at most 550 °C, refractive index (nd) of at least 1.83 and Abbe number (vd) of at most 26.0, which is represented, in term of atoms for making up the glass, by the following chemical composition (wt %):

P_2O_5	15.0 to 30.0 %
B_2O_3	0 to 4.0 %
GeO_2	0 to 12.0 %
Sum of $P_2O_5 + B_2O_3 + GeO_2$	17.0 to 30.0 %
Li_2O	0 to 5.0 %
Na_2O	5.0 to 13.0 %
Sum of $Li_2O + Na_2O$	5.0 to 14.0 %
Nb_2O_5	25.0 to 45.0 %
WO_3	0 to 20.0 %
Bi_2O_3	6.0 to 30.0 %
BaO	0 to 15.0 %

3. A precision molded optical glass article when comprising a glass as claimed in claim 1 or claim 2.

FIG. 1


COMPARISON OF COLORATION (TRANSMITTANCE)
EXAMPLE 9
COMPARATIVE EXAMPLE 3
TRANSMITTANCE (%)
100
90
80
70
60
50
40
30
20
10
0
200
300
400
500
600
700
WAVELENGTH (nm)